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(19)

(54) SELF-ADHERING PACKAGING AND WRAPPING MATERIALS

(71) We, DAUBERT CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Illinois, United States of America, of 709 Enterprise Drive, Oak Brook, State of Illinois, 60521, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to self-adhering, flexible packaging and wrapping sheet materials. In particular, the present invention relates to self-adhering, or "cold seal" type, flexible packaging and wrapping sheet materials which incorporate corrosion inhibitors.

While prior attempts heretofore have been made to develop a commercially acceptable self-adhering, or "cold seal" type, packing or wrapping sheet material having a corrosion inhibitor incorporated therein, so far as is known, none of these prior attempts has given rise to a satisfactory product. Sheet materials that have been produced as a result of these earlier efforts have usually comprised a flexible backing sheet having a functional coating in the form of a rubber-based adhesive on one side thereof. The functional coatings of these prior materials have a number of shortcomings, chief among which is their sensitivity to ultra-violet light, their inability to accept vapor phase corrosion inhibitors without undergoing some decomposition, their tendency to initiate the formation of "black" corrosion on ferrous metals under mildly humid conditions, and their proclivity to undergo discoloration and to show increased adhesion with respect to objects, especially metal objects, in contact therewith when stored for a prolonged period.

In accordance with the present invention, self-adhering, flexible packaging and wrapping sheet materials are provided which have none of the aforementioned disadvantages. The functional coatings of the packaging and wrapping sheet materials of this invention, while manifesting none of the objectionable properties of the rubber-based adhesives, have excellent self-blocking properties. The packaging and wrapping sheet materials of the present invention can be manufactured with conventional equipment, and the functional coatings of the materials can be formulated to meet the specifications of substantially any user.

Briefly, the self-adhering, flexible packaging and wrapping sheet materials of this invention comprise a flexible backing sheet having a functional coating adhered or bonded to one surface thereof. The backing sheet can be plastics materials such as polyethylene and polyester films such as "Mylar", foils, kraft papers, or corrugated papers. ("Mylar" is a Registered Trade Mark). The functional coatings of the packaging and wrapping sheet materials comprise a copolymer, or mixtures of copolymers, or mixtures of a copolymer and a homopolymer, formed from monomers selected from acrylic and methacylic acid esters of C_1—C_{18} alkyl alcohols, and vinyl esters and vinyl alkyl ethers, especially vinyl lower alkyl (C_1—C_7) ethers, and mixtures thereof. The functional coatings formed from the copolymer or the said mixtures, are characterized in part in that they have a theoretical glass transition temperature in the range of −20°C to 15°C, especially desirably −10°C to 10°C. The theoretical glass transition temperature can be readily calculated from the so called WLF (Williams—Landel—Ferry) equation,

$$\frac{1}{T_{g0}} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}} + \ldots + \frac{X_n}{T_{gn}}$$

where: T_g is a symbol describing the glass transition temperature in degrees Kelvin,

X is a symbol describing the weight fraction of monomer;

subscripts " 1, 2 to n " represent the specific monomer selected; and

subscript "0" represents the copolymer prepared from the monomers selected.

As can be seen, the equation relates the weight fractions of each constituent monomer (X_1, X_2...X_n) to the inverse of the glass transition temperature of the homopolymer made from the monomer (T_{g1}, T_{g2} ... T_{gn}). Each of the glass transition temperatures of the homopolymers is determined on a high molecular weight polymer prepared solely from the monomer selected. Functional coatings having a glass transition temperature in the range specified can be formulated from mixtures of copolymers, and mixtures of copolymers and homopolymers, wherein the copolymers and the homopolymers each have a glass transition temperature which falls outside the range called for, but which, when mixed, provide a functional coating falling within the range desired. In this same connection, it should be noted that the glass transition temperature of the functional coatings can be altered to meet the aforementioned desideratum by theaddition of various supple desideratum by the addition of various supplemental ingredients such as plasticizers, modifying resins and fillers, for example. In any event, irrespective of the manner in which a functional coating is formulated to give it a glass transition temperature within the range stated, the final coating should have high self-blocking properties and show substantially no adhesion with respect to objects packaged or wrapped in the materials of this invention, and should, furthermore, be stable to ultra-violet light, be able to accept corrosion inhibitors without undergoing decomposition, cause no discoloration of metal objects with which it comes into contact, and be resistant to discoloration and degradation upon long storage. Further in this same connection, it should be understood that the functional coatings of the sheet materials of the present invention are to be distinguished from pressure sensitive adhesives in that the latter have a glass transition temperature below $-30°C$, more usually, below $-40°C$. Similarly, rubber-based adhesives have a glass transition temperature of about $-60°C$.

The acrylic and methacrylic acid esters of C_1—C_{18} alkyl acohols useful in the practice of the present invention include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, lauryl methacrylate, and stearyl methacrylate.

Exemplary of vinyl esters and vinyl alkyl ethers useful in the formulation of the functional coatings are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl methyl ether, vinyl ethyl ether, vinyl butyl ether, vinyl isobutyl ether and vinyl propyl ether.

The preparation of the copolymers and homopolymers used in the formulation of the functional coatings can be carried out in accordance with known techniques. The preferred method of preparing the copolymers is solution polymerization involving the use of a solvent and a free radical catalyst. As stated, various supplemental ingredients such as plasticizers, modifying resins and fillers may be incorporated into the polymers to provide functional coatings having the required properties.

The coatings advantageously are applied to backing sheet materials in the form of solvent solutions. Standard techniques can be used for this purpose. Adhesion promoters can, if desired, be incorporated into the solvent solutions to improve adhesion of the functional coatings to the backing sheet substrate. Primer coatings, applied to the backing sheet, also can be employed where called for.

As indicated hereinabove, the packaging and wrapping sheet materials of this invention are especially useful for inhibiting the corrosion of metals or metal articles which are wrapped or otherwise enclosed in them. To this end, corrosion inhibitors, either of the vapor phase or the contact type, or both, advantageously are incorporated into the functional coatings of the materials. The nature of the corrosion inhibitor used, of course, will depend upon the metal to be protected. Thus, where ferrous metal articles are to be packaged or wrapped in the sheet materials, the corrosion inhibitor can be selected from a wide and extensive group of vapor phase and contact corrosion inhibitors which will provide the protection desired. Included in this group are volatile amine salts of fatty acids such as dicyclohexylammonium palmitate and dicyclohexylammonium pelargonate; volatile amine aromatic carboxylates exemplified by dicyclohexylammonium benzoate, diisopropylammonium benzoate, 2-butylamine benzoate and morpholinium benzoate, organic amine nitrite salts such as dicyclohexylamine nitrite, morpholine nitrite, diisopropylamine nitrite and guanidine nitrite; mixture of C_6 to C_{16} alkanoic acids and C_7 to C_{11} aromatic monocarboxylic acids as disclosed in U.S. Patent No. 3,080,211; as well as other well known inhibitors typical examples of which are 2-nitrothiophene, 2-di-nitrothiophene,

sodium benozate, ammonium benzoate, and n-propylbenzoate; and compatible mixtures of the foregoing.

In those instances where the metals to be packaged or wrapped in the sheet materials of this invention are copper or copper-base alloys, corrosion inhibitors such as benzotriazole, 3 - anilino - 1,4 - diphenyl - 5-phenylimino-1,2,4-triazole, and compatible mixtures thereof, can be incorporated into the functional coatings. Protection for both ferrous metals and copper and copper-base alloys, as well as aluminum, zinc and zinc-base alloys, tin, cadmium, lead and magnesium can be attained by incorporating compatible mixtures of the various aforementioned corrosion inhibitors into the functional coatings.

The quantity of the corrosion inhibitor incorporated into the functional coatings is somewhat variable. The generally optimum objectives of the invention, however, are achieved with quantities of the order of 2% to 10%, preferably 3% to 5%, by weight, of the functional coating.

The following examples are illustrative of the packaging and wrapping sheet materials of the present invention. It will be understood that these examples are not intended to be limitative of the invention since numerous changes can be made therein in the light of the guiding principles and teachings provided herein.

EXAMPLE I.

In a 3 neck flask, equipped with a condenser, 30g of ethyl acrylate, 21g of vinyl acetate, and 8.7g of 2-ethylhexyl acrylate were polymerized under nitrogen in 180g ethyl acetate with 0.18g of "vazo" (α,α - isobutyronitrile) initiator. Temperature was maintained between 65 and 80°C. After 8 hours of reaction 39g ethyl acrylate, 21g vinyl acetate, 6g 2-ethylhexyl acrylate and 0.18g of "vazo" were added to the above and temperature was maintained between the above limits for 4 hours. An additional 0.18g "vazo" was then added and the mixture heated for 6 hours more. Solid content of the copolymer at the end of polymerization was 39.4%, comprising by weight, 51.5% ethyl acrylate, 36% vinyl acetate, and 12.5% 2-ethylhexyl acrylate. The calculated Tg of the copolymer was −19°C.

The copolymer prepared as above was mixed with a commercial polymethacrylate having a calculated Tg of 33°C (Elvacite 2046) composed of a 50/50 copolymer of iso- and n-butyl methacrylates in ethyl acetate at a ratio of 4 parts of the prepared copolymer solids, to 1 part of polymethacrylate solids. Solids at end of dilution: 40%; the calculated Tg of the final mixture was −9°C.

The polymer composition thus prepared was coated on polyethylene and evaluated as a self-blocking coating, which does not adhere to other substrates. Rated for adhesion to itself, excellent; adhesion to other substrates, very poor (did not adhere). (Elvacite is a Registered Trade Mark).

EXAMPLE II.

79g of methyl acrylate and 30g of 2-ethylhexyl methacrylate are copolymerized at 80°C in 150g ethyl acetate solvent using 0.4g benzoyl peroxide as initiator. The resultant 44% solids solution was coated onto a variety of flexible backing materials and tested for self-blocking properties. The composition proved to have low adhesion to other substances together with high self-blocking properties. The calculated theoretical glass transition temperature of this composition is 7 degrees centigrade. The results for different compositions polymerized under similar conditions are tabulated below:

Methyl Acrylate (g)	2-Ethylhexyl Acrylate (g)	2-Ethylhexyl Methacrylate (g)	Tg °C	Adhesion to Metal	Self-blocking
70	0	30	7	Poor	Good
100	0	0	8	Poor	Poor
0	0	100	5	Poor	Poor

EXAMPLE III.

In another experiment three monomers were copolymerized in ethyl acetate using benzoyl peroxide as an initiator. The resultant solids solution was coated onto a variety of flexible backing materials as in Example II and tested for self-blocking properties. The ratios used and the results obtained are tabulated:

Ethyl Acrylate (g)	2-Ethylhexyl Acrylate (g)	Vinyl Acetate	Tg °C	Adhesion to Metal	Self-blocking
40	10	50	−3	Poor	Good
40	0	60	7	None	Good
50	0	50	2	Poor	Good

EXAMPLE IV.

70 parts of methyl acrylate and 30 parts of 2-ethylhexyl methacrylate are copolymerized at 80°C in 150 parts ethyl acetate using 0.4 part benzoyl peroxide as initiator. To the resultant composition are added 5 parts by weight of dicyclohexylammonium pelargonate. The calculated theoretical glass transition temperature of the composition is 7°C. The composition was coated onto a variety of flexible backing materials, including polyethylene, "MYLAR" and 30 lb. bleached kraft paper, and tested for self-blocking properties. The composition proved to have low adhesion to metals and high self-blocking properties.

EXAMPLE V.

The copolymer of Example IV is prepared as described. 5 parts by weight of benzotriazole are incorporated with the copolymer. The calculated theoretical glass transition temperature of the final composition is 7°C. The composition is coated on a "MYLAR" backing sheet and tested for self-blocking properties. The composition showed low adhesion to various metals and high self-blocking properties.

EXAMPLE VI.

A polymer composition is prepared as described in Example I. The following corrosion inhibitors are added to portions of the composition in an amount equivalent to 5% by weight based on solids, and the resulting compositions are coated on polyethylene film.

1. Dicyclohexylammonium caprylate (added as a 50% solids grind in isopropyl
2. Dicyclohexylammonium benzoate (added as a 50% solids grind in isopropyl alcohol)
3. Morpholinium benzoate (added directly)
4. Dicyclohexylammonium palmitate (added as a 50% solution in isopropyl alcohol at 50°C)
5. Sodium benzoate (added as a water-isopropyl alcohol solution)

The resulting compositions have excellent self-blocking properties and do not adhere to metal surfaces.

The corrosion inhibition properties of the sheet materials coated as described are evaluated by the following test: Steel strips, 1″ × 4″ are sealed in pouches formed from sheet materials having a functional coating of the polymer containing the corrosion inhibitors 1 through 4, while a similar strip is wrapped in a sheet having a functional coating containing the corrosion inhibitor numbered 5. The pouches, and the wrapped strip, are then placed in an enclosure at 100% relative humidity at 100°F for 1 week. No corrosion or discoloration is observed on any of the strips.

WHAT WE CLAIM IS:—

1. A flexible packaging or wrapping sheet material comprising a flexible backing having coating firmly bonded to one surface thereof, said coating comprising a copolymer, or a mixture of copolymers, or a mixture of a copolymer and a homopolymer, formed from monomers selected from acrylic and methacylic acid esters of C_1—C_{18} alkyl alcohols, and vinyl esters and vinyl alkyl ethers, and mixtures thereof, said copolymer or mixtures being characterized in that they have a theoretical glass transition temperature in the range of −20°C to 15°C, said coating being characterized in that it has high adhesion to itself and being further characterized in that it is stable to ultraviolet light and resistant to discoloration and degradation upon long storage.

2. A flexible sheet material according to claim 1 wherein a corrosion inhibitor is incorporated into the adhesive coating to provide protection against corrosion for metal articles packaged or wrapped in the material.

3. A flexible sheet material according to claim 2 wherein the corrosion inhibitor comprises 2% to 10%, by weight, of the coating.

4. A flexible sheet material according to claim 1 wherein the coating has a glass transition temperature in the range of −10°C to 10°C.

5. A flexible sheet material according to claim 2 wherein the corrosion inhibitor is a vapor phase corrosion inhibitor, a contact corrosion inhibitor, or a compatible mixture thereof.

6. A flexible sheet material according to claim 1 wherein the acrylic and methacrylic acid ester monomers are selected from methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate,, ethyl meth-

acrylate, butyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, lauryl methacrylate and stearyl methacrylate.

7. A flexible sheet material according to claim 1 wherein the vinyl ester and vinyl alkyl ether monomers are selected from vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl methyl ether, vinyl ethyl ether, vinyl butyl ether, vinyl isobutyl ether and vinyl propyl ether.

8. A flexible sheet material according to claim 1 wherein the coating comprises a mixture of (a) a copolymer comprising, by weight, about 51.5% ethyl acrylate, about 36% vinyl acetate, and about 12.5% 2-ethylhexyl acrylate, and (b) a copolymer comprising, by weight, about 50% isobutyl methacrylate and about 50% n-butyl methacrylate, the proportion of (a) and (b) in the mixture being about 4 of (a) to about 1 of (b).

9. A flexible sheet material according to claim 1 wherein the coating comprises a copolymer of about 70%, by weight, methacrylate and about 30%, by weight, 2-ethylhexyl methacrylate.

10. A flexible sheet material according to claim 2 wherein the coating contains a corrosion inhibitor selected from dicyclohexylammonium caprylate, dicyclohexylammonium palmitate, dicyclohexylammonium pelargonate, dicyclohexylammonium benzoate, diisopropylammoinium benzoate, 2-butylamine benzoate, morpholinium benzoate, dicyclohexylamine nitrite, morpholine nitrite, diisopropylamine nitrite, guanidine nitrite, mixtures of C_6 to C_{16} alkanoic acids and C_7 to C_{11} aromatic monocarboxylic acids, 2-nitrothiophene, 2-dinitrothiophene, sodium benzoate, ammonium benzoate, n-propylbenzoate, benzotriazole, and compatible mixtures thereof.

11. A flexible sheet material as claimed in claim 8 wherein the coating contains from 3% to 5% by weight, of a corrosion inhibitor selected from dicycylohexylammonium caprylate and dicyclohexylammonium palmitate.

12. A method of making a self-adhering, flexible packaging or wrapping sheet material having a coating which has high adhesion to itself and substantially no adhesion with respect to objects or articles packaged or wrapped in the sheet material, comprising forming a polymeric composition consisting essentially of a copolymer, or a mixture of copolymers, or a mixture of a copolymer and a homopolymer, formed from monomers selected from acrylic and methacrylic acid esters of C_1—C_{18} alkyl alcohols, and vinyl esters and vinyl alkyl ethers, and mixtures thereof, said copolymer or mixtures being characterized in that they have a theoretical glass transition temperature in the range of −20°C to 15°C, applying said polymeric composition to a flexible backing sheet material to form a coating thereon which is characterized in that it has high adhesion to itself, and being further characterized in that it is stable to ultraviolet light and resistant to discoloration and degradation upon long storage.

13. A method according to claim 12 wherein a corrosion inhibitor is incorporated into the polymeric composition.

14. A method according to claim 12 wherein the backing sheet material is a flexible plastics sheet material.

15. A flexible sheet material as claimed in claim 1 and substantially as hereinbefore described in any one of the foregoing specific Examples.

16. A method as claimed in claim 12 and substantially as hereinbefore described in any one of the foregoing specific Examples.

17. A flexible sheet material as claimed in claim 1 and whenever obtained by a method as claimed in any one of claims 12 to 14 or in claim 16.

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